

A NEW REACTION MODE OF METAL CARBONYL ANIONS:
OXYGEN ABSTRACTION BY ORGANOSILICON HALIDES

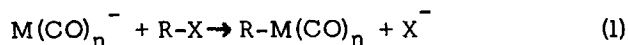
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Metal carbonyl anions, owing to their nucleophilic character, have enjoyed widespread use as intermediates in the synthesis of substituted metal carbonyls (1):



Germanium and tin halides react according to eq. 1 with a wide variety of metal carbonyl anions (2,3,4). In contrast, organo-silicon halides form silicon metal bonds only with $(\pi-C_5H_5)Fe(CO)_2^-$ (5,6); in all other cases, only ill-defined reactions were reported. Since a mild route to metal-silicon bonds was needed in connection with other research (7), an investigation of these anomalous reactions was initiated.

It has been found that in those reactions which did not lead to metal-silicon bonds, the only silicon compound isolated was invariably the disiloxane. Since these reactions are conducted in carefully dried tetrahydrofuran (THF) under nitrogen, the only source of oxygen is the carbonyl groups of the anion^{*}. The generality of this

*It is considered highly unlikely that oxygen would be abstracted from the THF solvent.

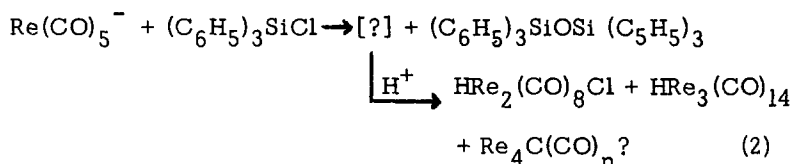
reaction is quite astonishing and represents an unexpected mode of reaction for metal carbonyl anions. A variety of carbonyl-containing species is produced, and these mixtures are not completely characterized at present.

Thus, triphenylchlorosilane reacts with NaMn(CO)_5 in THF to give hexaphenyldisiloxane (52%) and a red, anionic species as the major carbonyl component. Excellent crystals of the tetraethylammonium salt may be grown with the approximate composition $(\text{Et}_4\text{N})_2\text{Mn}_5(\text{CO})_{24}$ (calcd: C, 38.9; H, 3.34; N, 2.32; Mn, 22.7; Found: C, 38.4; H, 3.08; N, 2.37; Mn, 23.2). The IR spectrum of the above cluster-compound is essentially identical in acetone solution and in the solid (KBr disc). Carbonyl stretching bands are observed at 2049, 2039 w, 2014 m, 1980 vs, 1946-43 m doublet, 1904-1840 m doublet, and 1869 m (cm^{-1}), indicating a lack of bridging carbonyl groups. The compound is diamagnetic in solution (NMR technique) which means that either hydride ligands are present or the actual structure is even multiples of the empirical formula. No high-field signals were found in the NMR spectrum, but the solubility is so low that a weak signal could have been lost in the noise. Although the N : Mn ratio is well established, the elemental analyses are not precise enough to determine the exact number of carbonyl groups; hence, a crystal structure determination will be initiated.

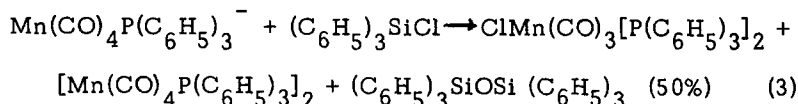
The reaction of NaRe(CO)_5 and triphenylchlorosilane gives a 95% yield of hexaphenyldisiloxane and a complex mixture of rhenium carbonyls. The mixture was acidified with phosphoric acid and chromatographed from alumina. The major components, identified

mass spectroscopically, are $\text{HRe}_3(\text{CO})_{14}$ (8), and the previously unreported $\text{HRe}_2(\text{CO})_8\text{Cl}$. The latter compound is assigned a structure with bridging H and Cl atoms on the basis of its fragmentation pattern (9), IR spectrum, and the fact that the structure, $(\text{CO})_4\text{Re} \begin{matrix} \text{H} \\ \leftarrow \text{ } \rightarrow \\ \text{Cl} \end{matrix} \text{Re}(\text{CO})_4$, provides each rhenium with the rare-gas configuration.

Under very high gain, weak peaks could be detected in one fraction (which was mostly $\text{HRe}_2(\text{CO})_8\text{Cl}$) arising from a Re_4 cluster (isotopic distribution calcd. for Re_4 : 1 : 2.4 : 2.1 : 0.8 : 0.1, obs. 1 : 2.5 : 2.4 : 1.0 : 0.2). The masses corresponded to the species $\text{Re}_4\text{C}(\text{CO})_x^+$ ($x = 0-4$). The parent ion was not observed because of the very low intensity of these peaks. No species of the type $\text{Re}_4(\text{CO})_x^+$ were observed, suggesting that the compound giving rise to the Re_4 ions is a rhenium-carbide cluster.



Reactions of some triphenylphosphine-substituted carbonyl anions with triphenylchlorosilane have also been studied. $\text{Na}[\text{Mn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3]$, prepared from the corresponding dimer, reacts to give the products shown in (3).



Although $\text{NaCo}(\text{CO})_4$ reacts in a very complex manner with $(\text{C}_6\text{H}_5)_3\text{SiCl}$ (giving among other products the disiloxane and CoCl_2), $\text{NaCo}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$ reacts to give trans- $(\text{C}_6\text{H}_5)_3\text{SiCo}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$ in 31% yield (ν_{CO} : 1950 cm^{-1} , dec. 180°). No hexaphenyldisiloxane

was observed.

Triphenylchlorosilane reacts with $(\eta\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\text{P}(\text{C}_6\text{H}_5)_3)\text{Na}$ to give a 50% yield of hexaphenyldisiloxane and $(\eta\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2\text{-P}(\text{C}_6\text{H}_5)_3\text{H}$ (38%)*. The hydride was identified by mass spectroscopic data (Parent ion mass = 476 for Mo^{92}) and elemental analysis. Infrared studies show that the hydride is not formed during the initial reduction, but appears rapidly after triphenylchlorosilane has been added to the anion. A second, as yet unidentified, metal carbonyl is also produced in this reaction.

Most of the reactions discussed give rather complex mixtures, and attempts to use column chromatography to separate the components have failed (some carbonyls react with the usual adsorbents even after they are vacuum dried and the column prepared under a nitrogen atmosphere). As a result, the products were separated by fractional crystallization, and all the compounds present in the mixtures could not be obtained sufficiently pure for identification. Hence, the fate of the carbon atom remaining after oxygen abstraction is largely unknown. Although disiloxanes have been observed to form when compounds of the type $\text{R}_3\text{Si-M}(\text{CO})_n$ are thermally decomposed (10), the mild conditions and rapidity of formation of the disiloxane in the above reactions indicate that silyl metallic compounds are not intermediates. Instead, the primary reaction probably involves nucleophilic attack by the carbonyl oxygen, and represents a heretofore unrecognized reaction path for

*The phosphine-substituted anion was prepared by sodium amalgam reduction of the previously unreported $[(\eta\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\text{P}(\text{C}_6\text{H}_5)_3)]_2$, which is prepared in high yield by adding cyclopentadienylmolybdenum tricarbonyl dimer to molten triphenylphosphine at 120° . $\nu_{\text{CO}} = 1980$ (w), 1900 (s), 1770 (s) cm^{-1} ; dec. 180° ; calcd.: C, 62.7; H, 4.22; P, 6.47; found: C, 61.2; H, 4.04; P, 6.31.

metal carbonyl anions.

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